

CERIA BASED NANO-SCALE CATALYSTS FOR WATER-GAS SHIFT (WGS) REACTION

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ABSTRACT

This paper describes our research efforts towards the preparation of high surface area ceria oxide (CeO₂) containing catalysts for fuel processing and therefore for fuel cells applications. In the present work, we present a simple, single step flame synthesis method to prepare high surface area ceria based fuel reformation catalysts using aqueous solutions of metal acetate precursors. The specific surface areas of the synthesized powders are in the range of 130 and 163 m²/g. High-resolution transmission electron microscopic (TEM) characterization showed that the particle sizes for the ceria materials are in the range of 3 and 10 nm. X-ray diffraction (XRD) and X-ray photoelectron spectra show the presence of transition metal oxide in the as prepared catalysts. The catalysts also test for water-gas-shift (WGA) reaction.

INTRODUCTION

The Army's Transformation demands a more responsive, deployable, agile, versatile, lethal, survivable, and sustainable force. This transformation will result in a Future Force, which will require power for highly mobile vehicles, auxiliary power unit (APU), unattended ground networked sensors, and individual War-fighter. Fuel cell is one of most favorable technologies for power and energy source for the Army's Transformation. Polymer electrolyte membrane fuel cells (PEMFCs) has received much attention for automotive and APU applications. In recently years, PEMFC for automotive applications has also been tremendously improved. However, a reliable and safe hydrogen source is a key barrier for PEMFC technology practical applications.

PEMFCs are highly sensitive to carbon monoxide (CO), even a trace amount of carbon monoxide is poisoning PEMFCs. Carbon monoxide is one of a products produced in the hydrocarbon reformation. The water-gas shift (WGS) reaction ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$) is used to convert carbon monoxide

and water to hydrogen and carbon dioxide. The presence of a suitable catalyst in the WGS reaction can reduce the concentration of CO down to 10 ppm.

Recently it has been reported that transition metal supported ceria increases the rate of WGS reaction as compared to the commercial WGS catalysts because of the high oxygen storage capacity of ceria, mobility of oxygen and dispersion of transition metal on the ceria surface. Cerium oxide (CeO₂)/ceria is an important inorganic material having the cubic fluorite type crystal structure (1). Ceria either in the pure form or doped with other metals (Cu, Ni, etc) / metal ions (Mg²⁺, La²⁺, Sc²⁺, Gd³⁺, Y³⁺, Zr⁴⁺ etc.), potentially has a wide range of vast applications including gas sensors (2), electrode materials for solid oxide fuel cells (3, 4) oxygen pumps, amperometric oxygen monitors and three way catalytic supports for automobile exhaust gas treatment (5,6).

Nano-crystalline particles have attracted much attention because of their improved physical and chemical properties compared to those of bulk materials. Various solution-based techniques have been used for the preparation of pure ceria and transition metals, rare earth metals, or metal ions doped ceria materials, including coprecipitation (7, 8), hydrothermal (9-11), microemulsion (12, 13), sol-gel (14), solution combustion (15) and electrochemical methods (16). In addition, solid-state reaction, mechano-chemical methods, chemical vapor deposition (CVD), sputtering have also been used to make ceria-based materials (17-19). These methods are either multi step and time-consuming (e.g. solution based techniques) or control of the product composition may be difficult (e.g. CVD).

In the present paper we report a single step alternative route for synthesizing CeO₂ based nanoparticles. The process involves the pyrolysis of aqueous solutions of the metal acetate without addition of any extra fuel in a methane oxygen flame. The CeO₂ catalysts also test for WGS reaction.

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EXPERIMENTAL

The precursors used were cerium acetate (Strem Chemicals, 99.9%) as the cerium source, copper acetate (Strem Chemicals, >98%) as the copper source, nickel acetate (Strem Chemicals, >98%) as the nickel source and iron acetate (Sigma-Aldrich Chemicals, >99.0%) as the iron source. The precursors were dissolved in deionized water to make 0.3 M solutions of each. For the transition metal supported ceria, a series of solutions have been prepared starting from 5, 10, 20, 30 and 40 mole % of transition metal in ceria. The solutions were filtered through a membrane filter before filling the nebulizer (Gemini Scientific Corporation, Inc.). Liquid precursor feed was then atomized with compressed air resulting in a fine spray. In the reactor the flame was made by methane, oxygen and nitrogen. The flow rate for each gas was methane 2.20 l/min, oxygen 1.81 l/min and nitrogen 3.7 l/min. The flow rate of the precursor solution into the flame was 0.5ml/min. After burning the fine spray, the particles were collected on a water-cooled surface by thermophoresis, which was kept on the top of the flame. The distances of the water-cooled surface from the burner and the flame were 6.5 cm and 2 cm respectively.

The synthesized materials were then characterized by powder X-ray diffraction (XRD) using $\text{CuK}\alpha$ ($\lambda = 1.5408\text{\AA}$) for the phase analysis and crystal structure determination. Thermogravimetric analysis (TGA) was used to determine the amount of unwanted materials such as water and carbonaceous compounds in the sample. Atomic bonding was analyzed using Fourier transformed infrared spectroscopy (FTIR). Brunauer, Emmett and Teller (BET) gas absorption method was applied to investigate the surface area of the sample. Transmission electron microscopy (TEM) was used for the particle size analysis and surface morphology of the material. X-ray photoelectron spectroscopy (XPS) was utilized to determine the oxidation state of the transition metal used in the ceria system.

RESULTS AND DISCUSSIONS

Thermogravimetric analysis (TGA) was performed in air at a heating rate of $10^\circ\text{C}/\text{min}$. The TGA curve (Fig. 1) for the pure ceria sample indicates that there were two stage of weight loss. The first weight loss (between 20 to 200°C) was due the removal of water molecules, which probably come from the condensation of water molecule on the water-cooled surface. The second stage weight loss (between 300 to 600°C) resulted from the burning and oxidation of carbon compounds (combustion by-product) likely from incomplete combustion of the metal acetate precursor, which is confirmed by FTIR (Fig. 2).

Similarly, the TGA of the as prepared Cu/CeO_2 showed the same weight loss behavior with the presence of more carbon in the sample.

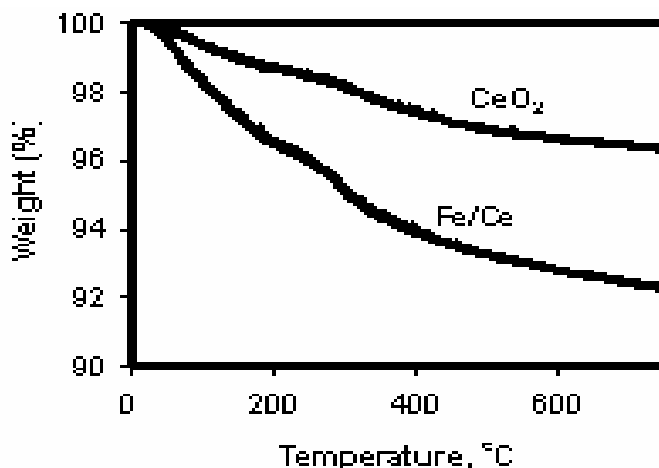


Fig. 1 Thermogravimetric analysis (TGA) of as prepared pure CeO_2 and 40% Fe/CeO_2 powder

Figure 2 shows the FTIR spectra in the region $400 - 4000\text{ cm}^{-1}$ of as prepared CeO_2 sample. The IR absorption bands in the region of $2800\text{--}2900\text{ cm}^{-1}$ are typical of the C-H stretching mode of hydrocarbons. The C=O stretching band at $\sim 1400\text{ cm}^{-1}$ confirms the presence of unburned acetic acid in the final product.

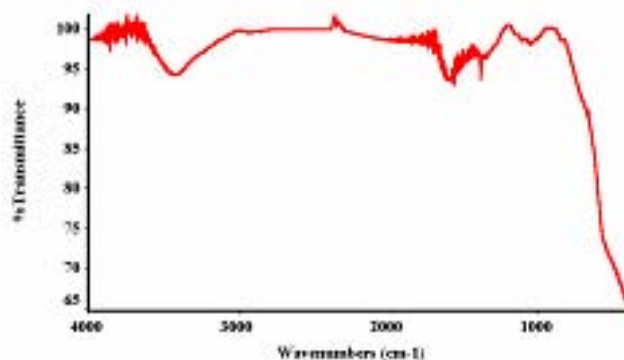


Fig. 2 Fourier transformed infrared spectra of the as prepared pure ceria

Residual water and hydroxyl group are detected with a large band at around 3500 cm^{-1} , corresponding to O-H stretching frequency, and a broad band at around 1600 cm^{-1} , due to the bending vibrations of associated water. Another species of strong bands is located at around 1000 cm^{-1} , which may be either associated with the formation of carbonate like species (20) or the formation of nanocrystalline CeO_{2-x} (21).

The X-ray diffraction (XRD) pattern of 40% Cu doped CeO_2 is shown in Fig. 3. The diffraction lines corresponding to the fluorite type structure and the d values agree well with those expected for CeO_2 . The peaks corresponding to Cu or CuO could not be detected even with the increase of Cu content. This suggests that metallic Cu or $\text{Cu}^{2+}/\text{Cu}^+$ may not be substituted for Ce^{4+} in CeO_2 . Increasing the Cu content increases the line width compared to the pure CeO_2 and the absence of Cu or Cu-oxide phase suggest that the metallic Cu or $\text{Cu}^{2+}/\text{Cu}^+$ ions are dispersed on the surface of CeO_2 . Diffraction patterns of Ni and Fe doped CeO_2 prepared by the flame synthesis method are similar to those of pure CeO_2 and Cu doped CeO_2 .

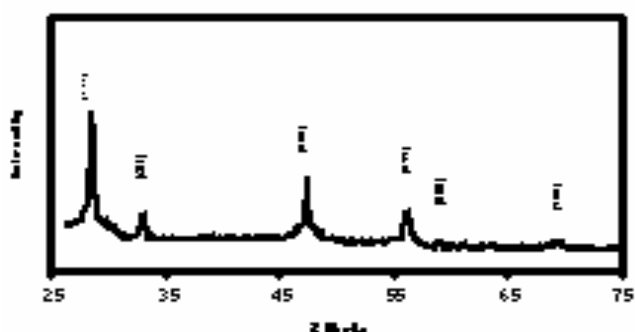


Fig. 3 X-ray diffraction spectra of the as prepared 40% Cu/ CeO_2 powder

X-ray photoelectron spectra (XPS) of 40% Ni/ CeO_2 in the Ce(3d) and Ni(2p) regions are given in Figure 4. The Ce(3d) spectrum with intense satellites marked in Figure 4 identifies with Ce^{4+} in CeO_2 (22). No significant peak is observed in the Ce(3d) spectrum corresponding to Ce^{3+} . The XPS of as prepared Ni($2p_{3/2}$) shows that Ni is in the +2 oxidation state as seen from the Ni+2 ($2p_{2/3}$) binding energy as well as the satellite peaks. The Ni/ CeO_2 catalyst after the water-gas shift treatment shows the zero oxidation state of Ni, which indicates the reduction of Ni^{2+} to Ni happens in the reducing atmosphere.

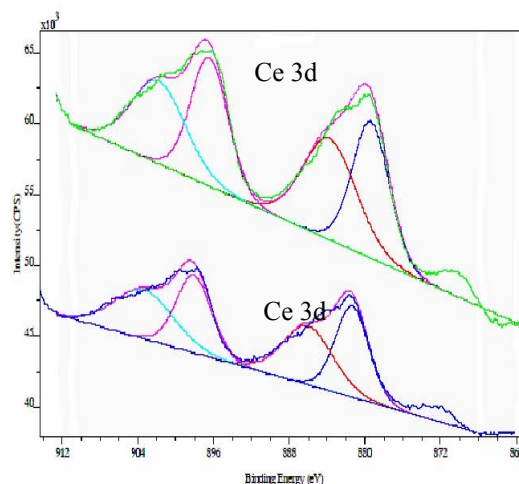
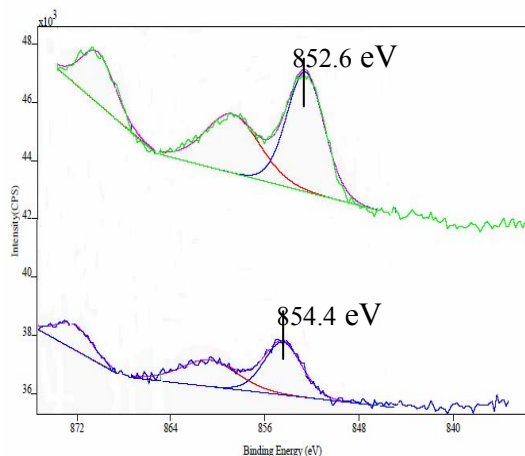


Fig. 4 X-ray photoelectron spectra of the as prepared and WGS treated 40% Ni/ CeO_2 powder

Transmission electron microscopic (TEM) image of 40%Cu/ CeO_2 is shown in Figure 5. The particles are spherical in size with particle size in the range of 3-5 nm. The absence of big particle suggests that the precursor droplets are vaporized completely in the flame. The selected area electron diffraction (SAED) pattern is index to polycrystalline CeO_2 in the fluorite structure and no line corresponding to Cu or any of the oxides of Cu is detected. This again suggests the dispersion of Cu^{2+} on the CeO_2 surface. A particle size and BET surface area analysis of pure ceria and M/ CeO_2 (M=Cu, Ni, Fe) is given in Table 1.

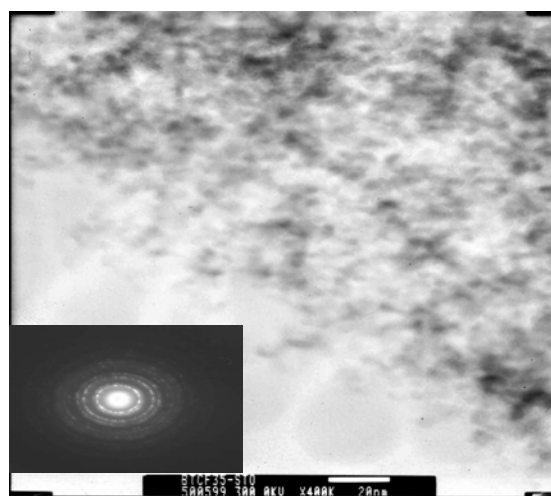


Fig. 5 Transmission electron micrograph and the selected area electron diffraction pattern of the as prepared Cu/ CeO_2 powder.

Table 1 Particle size and the BET surface area of the synthesized pure ceria and transition metal supported ceria.

Material	particle size (nm)	Surface area (m ² /g)
Pure CeO ₂	3-5	153
5% Cu/CeO ₂	3-5	135
10% Cu/CeO ₂	3-5	153
15% Cu/CeO ₂	3-5	128
30% Cu/CeO ₂	3-5	-
40% Cu/CeO ₂	3-10	156
40% Fe/CeO ₂	-	127
5% Ni/CeO ₂	5	163
40% NiCeO ₂	-	163

WATER-GAS-SHIFT (WGS) REACTION EXPERIMENTAL RESULTS

A comparison of the WGS activities on pure ceria, 40% Cu-ceria, 40% Ni-ceria and 40% Fe-ceria is shown in Fig. 6. The feed gas contains 5% CO and 5% H₂, and the H₂O/CO ratio is 5. The pressure drops were < 10 psig and the conversions were <10% for all the reported data. The water-gas shift activities of Cu-, Ni- and Fe-ceria are under H₂/CO ratio =1. Below 300°C, Cu-ceria has the highest shift activities at a given temperature while the Ni-ceria is more active than Fe-ceria. No methane formation is observed in any case. One may argue that the presence of H₂ activates the Cu-ceria by reduction of copper oxides into metallic copper. Additional tests are performed to identify the active copper species. The activity results of Cu-ceria with CO (Fig. 7) demonstrate that the active Cu species is present as prepared. In order words, there is no need to reduce the copper oxides with H₂ to create the active copper species for WGS reaction. The Cu-ceria is the most active, followed by Ni-ceria and Fe-ceria.

Figure 7 also illustrates the WGS activities of Cu-ceria under various conditions. The Cu-loading of 40% gives higher activities than 15%. The 15% Cu-ceria catalyst works at either H₂/CO ratio = 1 or 0. The H₂/CO ratio = 0 refers to 5% CO without H₂. The activity is higher in the absence of H₂. Annealing of the 40% Cu-ceria at 700 °C for 3 hours reduces its surface area. When we compare the activity of the annealed catalyst with that of the as-prepared catalyst, 700°C annealing increases the WGS activity for temperatures less than 250°C. Annealing at 1100°C reduces the activity dramatically. This heat treatment decreases the surface area of the catalyst and possibly

the size of the particles. Although surface area and crystallite size are generally believed to be two of the major factors for catalytic activities, dopants in Ce crystal structure also play critical roles in the WGS activity.

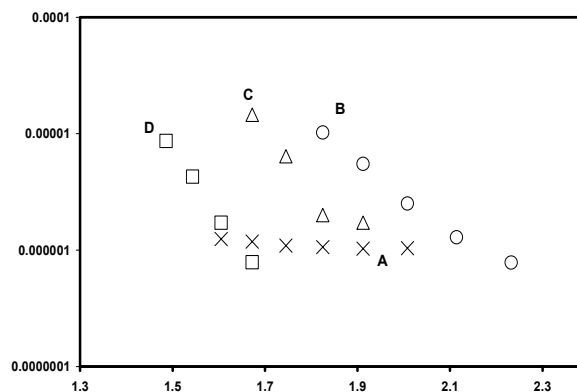


Fig. 6 Water-gas shift activities of various flame-made ceria-based catalysts, (A) Ceria (x), (B) 40% Cu-ceria (o), (C) 40% Ni-ceria and (D) 40% Fe-ceria (□). All measurements were taken with 5%H₂, 5% CO and H₂O/CO ratio =5.

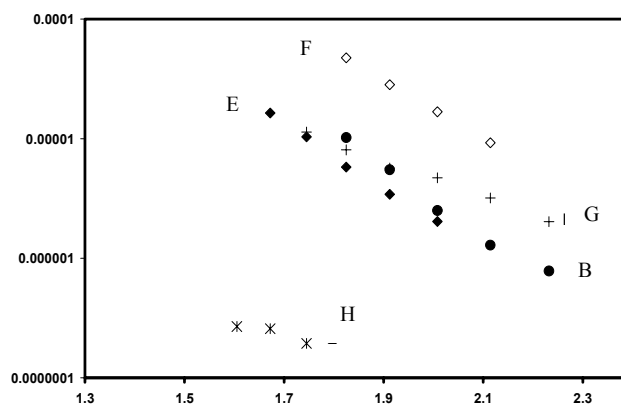


Fig. 7 Water-gas activities of various Cu-ceria catalysts, (B) 40% Cu with H₂/CO ratio =1, (E) 15% Cu with H₂/CO ratio =1, (F) 15% Cu with H₂/CO ratio =0, or 5% CO with no H₂, (G) 700°C annealed 40% Cu with H₂/CO ratio =1, and (H) 1100°C annealed 40% Cu with H₂/CO ratio =1. All measurements were taken with H₂O/CO ratio =5.

The significance of this work is that we have developed a non-pyrophoric low temperature WGS catalyst for fuel processor. Our catalysts have three important characteristics. First, there is no need to use metal chloride precursors to prepare the catalysts in flame synthesis method. Any residual chloride may

poison the fuel cell catalysts downstream. Second, all the catalysts shown in Figure 6 are not sensitive to air (i.e. non-pyrophoric) while commercial typical Cu/ZnO/Al₂O₃ catalysts are air sensitive. In contrast to industrial plants, this feature is particularly important for fuel processing applications because these applications involve frequent on-off cycles during which air enters the system. Using non-pyrophoric materials often means a safer system. Another important characteristic is that our catalysts show high activities at H₂/CO ratio = 1. Previously, most of the water-gas shift catalyst research projects focus on gas feed at very low or in absence of hydrogen. Only recently the literature shows interests in the water-gas shift catalyst that works at a reasonable hydrogen level (relative to CO). It should be noted that hydrogen is the main fuel for fuel cell applications, particular polymer electrolyte membrane (PEM) fuel cells. Fuel processors break down the hydrocarbon fuel into reformat which contains smaller molecules including H₂, CO and others. Here we have tailored our catalysts at H₂/CO =1 which is realistic for catalytic partial oxidation of hydrocarbons fuel.

CONCLUSION

Flame synthesis is an easy, single step method for the preparation of pure CeO₂ and the transition metal doped CeO₂ materials starting from aqueous solution of metal salts. The process is time and possibly cost efficient compared to other wet chemical methods. From XPS it is clear that the transition metals in the CeO₂ are in an oxidized state and the metal ions may be on the surface of the CeO₂ lattice. Preliminary results show that the flame made transition metals doped CeO₂ powders are active for the water-gas shift reaction (22). A small amount of carbon is present in the as prepared sample, which is confirmed by TGA and FTIR. The particle sizes of the synthesized materials are in the range of 3-10 nm and the BET surface areas are in the range of 127-163 m²/g.

The flame-made Fe, Ni and Cu/CeO₂ catalysts are evaluated as the water-gas shift catalyst. Cu/CeO₂ showed highest activities among these flame-made catalysts.

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REFERENCES

1. M. Hirano, M. Inagaki, J. Mater. Chem., 10 (2000) 473
2. B.C.H. Steele, Solid State Ionics, 129 (2000) 95
3. T. Kubo, H. Obayasi, J. Electrochem. Soc., 122 (1975) 42
4. H. Yahiro, Y. Bab, K. Eguchi, H. Arai, J. Electrochem. Soc., 135 (1988) 2077
5. P. Fornasiero, G. Balducci, R. DiMonte, J. Kaspar, V. Sergo, G. Gubitosa, A. Ferrero, G. Maziani, J. Catal., 164 (1996) 173
6. G.R. Rao, P. Fornasiero, R. DiMonte, J. Kaspar, G. Vlaic, G. Balducci, S. Meriani, G. Gubitosa, A. Cremona, M. Graziani, J. Catal., 162 (1996) 1
7. J. Van herle, T. Horita, T. Kawada, N. Sakai, H. Yokokawa, M. Dokiya, J. Am. Ceram. Soc., 80 (1997) 933
8. K. Higashi, K. Sonoda, H. Ono, S. Sameshima, Y. Hirata, J. Mater. Res., 14 (1999) 957
9. M. Hirano, E. Kato, J. Am. Ceram. Soc., 82 (1999) 786
10. P. Shuk, M. Greenblatt, Solid State Ionics, 116 (1999) 217
11. Y.C. Zhou, M.N. Rahaman, J. Mater. Res., 8 (1993) 1680
12. A. Martinez-Arias, M. Fernandez-Garcia, V. Ballesteros, L.N. Salamanca, J.C. Conesa, C. Otero, J. Soria, Langmuir, 15 (1999) 4796
13. T. Masui, K. Fujiwara, Y.M. Peng, T. Sakata, K. Machida, H. Mori, G. Adachi, J. Alloys. Compd., 269 (1998) 116
14. L. Li, X. Lin, G. Li, H. Inomata, J. Mater. Res., 16 (2001) 3207
15. P. Bera, S.T. Aruna, K.C. Patil, M. S. Hegde, J. Catal., 186 (1999) 36
16. Y. Zhou, R.J. Phillips, J.A. Switzer, J. Am. Ceram. Soc., 78 (1995) 981
17. X.R. Ye, D.J. Jia, J.Q. Yu, X.Q. Xin, Z. Xue, Adv. Mater., 11 (1999) 941
18. W. Bai, K.L. Choy, N.H.J. Stelzer, J. Schoonman, Solid State Ionics, 116 (1999) 225
19. M. Hasegawa, Y. Kato, M. Kagawa, Y. Syono, J. Mater. Sci. Lett., 15 (1996) 1608
20. D. Terribile, A. Trovarelli, J. Llorca, C.D. Leitenburg, G. Dolcetti, J. Catal., 178 (1998) 299
21. J.Y. Ying, A. Tschöpe, The Chem. Engg. J., 64 (1996) 225
22. I. C. Lee, R.K. Pati, S.H. Ehrman, D. Chu, (Unpublished work).